(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 379 312 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 90300349.9

(22) Date of filing: 11.01.90

(51) Int. Cl.5: C11D 3/395, D06L 3/04, C09B 47/32

(30) Priority: 14.01.89 GB 8900807

(43) Date of publication of application: 25.07.90 Bulletin 90/30

(84) Designated Contracting States: ES GB GR IT

(71) Applicant: The British Petroleum Company p.l.c.
Britannic House Moor Lane
London EC2Y 9BU(GB)

(72) Inventor: Callaghan, Ian Charles
The British Petroleum Co. p.l.c. Chertsey Road
Sunbury-on-Thames Middlesex TW16 7LN(GB)
Inventor: Masheder, David
The British Petroleum Co. p.l.c. Chertsey Road
Sunbury-on-Thames Middlesex TW16 7LN(GB)

(74) Representative: Ryan, Edward Terrence et al
BP INTERNATIONAL LIMITED Patents & Agreements Division Chertsey Road
Sunbury-on-Thames Middlesex, TW16 7LN(GB)

(54) Photobleach compositions and processes for making them.

(57) A water-insoluble photobleach is substantially free of water-soluble photobleach. It may be made by reacting a water-soluble photobleach with a long chain quaternary nitrogen compound. Laundry detergents containing the photobleach have reduced tendency to stain washing.

EP 0 379 312 A1

PHOTOBLEACH COMPOSITIONS AND PROCESSES FOR MAKING THEM

The present invention relates to photobleach compositions.

Photobleaches are materials included in detergent laundry compositions intended for use in parts of the world with high incident sunlight. They produce a bleaching effect on laundry on being exposed to sunlight when the laundry is dried in the open air.

Examples of such bleaches have been disclosed in various patent specifications. GB1 372 035 discloses a bleaching process in which textiles are treated with a detergent composition containing photoactivators and exposed to light. Among the photactivators mentioned are porphyrins and phthalocyanines with anionic substituents, which may be zinc phthalocyanines.

GB 1 408 144 discloses a similar process in which a peroxy compound is used to provide a source of oxygen additional to that provided by oxygen from the atmosphere.

US 4 033 718 discloses a textile bleaching process which is similar to those described above, but which uses a specific mixture of sulphonated zinc phthalocyanines.

US 4 166 718 discloses a process for bleaching textiles by oxygen in the presence of light using a photactivator which is a water-soluble aluminium phthalocyanine. The specification indicates that water-solubility is necessary for a photoactivator.

US 4 648 992 discloses novel water-soluble phthalocyanine compounds which may be used as photobleaching agents. Various elements are listed among the central atoms which may be present.

Conventional photobleaching compositions contain compounds which are closely related to substances which are used as fabric dyes. This does not cause problems when the compositions are used in normal wash liquids (i.e. the dilute aqueous medium in which clothes are washed). However, persons washing laundry with localised stains or dirt (spots) are often in the habit of applying a concentrated solution of detergent to the spots before the main wash. This application of a concentrated solution to a spot is particularly likely to occur if the detergent composition is supplied to the user as a liquid detergent concentrate rather than a powder. If concentrated solutions of conventional photobleaches are applied to textiles then staining of the textiles is likely to result. This staining is not removed by the subsequent washing step in the dilute wash liquid.

As indicated above materials which have been proposed as photobleaches (i.e. materials which activate oxygen in the presence of light to give a bleaching action) have similarities with materials proposed for use as dyestuffs. The materials used as photobleaches have been water-soluble. Some dyestuffs, in contrast, have been used in organic solvents such as ethanol. US 2 150 741 discloses a method of converting an aqueous solution of a phthalocyanine dyestuff into coloured salts which are insoluble in water by reaction with a long chain aliphatic cationic compound. The specific phthalocyanine compounds mentioned are nickel and copper phthalocyanines. These are known not to have photobleach activity. They have a high affinity for textiles as they are manufactured as dyes and therefore would not be suitable for use as photobleaches, even in dilute solution, as photobleaches are intended to bleach fabric not to dye it. For reasons of cost household laundry detergents are intended for use in aqueous systems. There is no interest in using a system which requires ethanol as solvent as disclosed in US 2 150 741 in household laundry detergents and of course there is no interest in using a dye.

There is need for a photobleach which can be used in laundry detergents without causing staining problems when used at high concentrations.

According to the present invention there is provided a photobleach which is a substantially water-insoluble photobleach substantially free of water-soluble photobleach.

According to another aspect of the present invention a laundry detergent composition comprises a photobleach consisting of a substantially water-insoluble photobleach substantially free of water-soluble photobleach.

The novel photobleach material of the present invention is water-insoluble in the sense that it is substantially free of constituents which are soluble in pure water and which can thus produce undesirable staining. Nevertheless the material is dispersible in the dilute wash liquid in which the main washing action takes place.

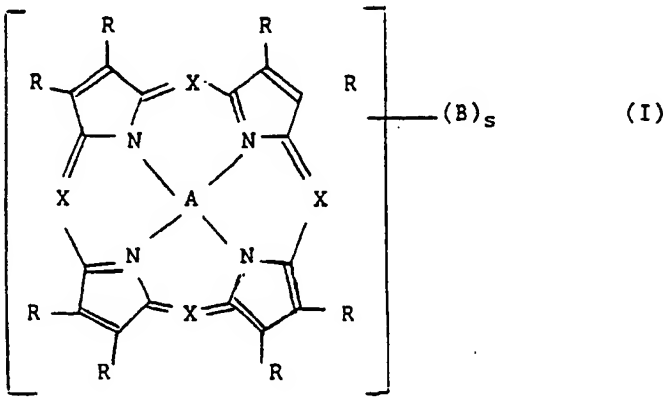
The substantially water-insoluble photobleach is preferably an insoluble quaternary nitrogen salt of a water-soluble photobleach.

The insoluble quaternary nitrogen salt is formed from a relatively high molecular weight quaternary nitrogen compound which is sufficiently soluble in water to allow it to be dissolved to give an aqueous reactant solution but which reacts with the other component to give an insoluble precipitate. The solubility of the water-soluble quaternary salt will be affected by the counter anion and a preferred counter anion is the

chloride ion. Among other counterions which can be used are the methylsulphate ion. The quaternary nitrogen compound may be a quaternary ammonium compound or may be a quaternary imidazolidinium compound. Examples of suitable quaternary nitrogen compounds are the quaternary nitrogen compounds containing one or two long chain alkyl groups (e.g. from C10 to C22). A specific compound which can be used is di(hydrogenated tallow) dimethylammonium chloride.

The other component which forms the water-insoluble ammonium salt is a water-soluble photobleach. As indicated above such photobleaches are well-known. Photobleaches are selected so as not to have a high affinity ("substantivity") for textile fibres which can cause colouration when photobleach is used at low dilutions. A preferred class of water-soluble photobleaches is constituted by the anionically-substituted porphines. The porphine may be metallated for example with Zn(II), Al(III), Ca(II), Cd(II), Mg(II), Sc(III), Sn-(IV), or Fe(II).

The porphines may be defined by the formula:



(I)

in which

1) each X is =N- or =CY- and the number of =N- groups is 0 or an integer of from 1 to 4 inclusive, and

2) each Y, independently, is either H or alkyl, cycloalkyl, aralkyl, aryl, aralkyl, or heteroalkyl, and

3) wherein each R, independently, is either

a) H or

b) alkyl, cycloalkyl, aralkyl, aryl, alkaryl, or heteroalkyl, or

c) wherein adjacent pairs of R are joined together with ortho arylene groups to form alicyclic or heterocyclic rings; or wherein

4) A is 2 H atoms bonded to diagonally opposite N atoms, or is Zn(II), Cd(II), Mg(II), Ca(II), Al(III), Sc-(III), Sn(IV) or Fe(II); wherein

5) B is an anionic group substituted into Y or R, and s is the number of such anionic groups.

The preferred porphine compounds are the tetraaza tetrabenzo derivatives, namely the phthalocyanines i.e. those compounds in which X is N in formula (I) above and adjacent pairs of R are joined together to form benzene rings.

The substantially water-insoluble salt may be formed by the reaction of aqueous solutions of the starting materials. The precipitated product may be sufficiently free of water-soluble fabric substantive materials capable of causing staining to be used in detergent compositions without further treatment. However, it may be free of soluble coloured components. It may be desirable to subject the precipitate to a solvent extraction step with a hydrophobic solvent (e.g. carbon tetrachloride) to recover a solution of the desired material before removing the solvent and carrying out a water washing step.

The photobleach material of the present invention may be incorporated into laundry detergents, but is particularly suitable for incorporation into liquid laundry detergents.

It is particularly preferred to add the photobleach material to a liquid laundry detergent in the form of a pre-dispersion in a non-ionic surfactant, for example a C_{12}-C_{15} alkyl ethoxylate.

Formulations for laundry detergents, both powder and liquid, are well-known to those skilled in the art and there is therefore no need to give details here.

The quantities of photobleach which may be incorporated into detergent compositions may for example be in the range 0.01 to 0.5% wt based on the weight of the powder or liquid sold to the consumer.

The invention will now be illustrated by reference to the following experiments in which examples of the invention are identified by number and comparative tests, not according to the invention, are identified by letters.

Example 1

The Preparation of the photobleach

The starting material for the preparation was Tinolux BBS ("Tinolux" is a trade mark). This is a commercially available water-soluble photbleaching compound supplied by Ciba-Geigy as a ca. 10% by weight solution in water. Tinolux BBS is a tetrabenzotetraaza porphine believed to be an A1 salt of a water-soluble phthalocyanine made in accordance with US 4 166 718.

30g of the solution of the phthalocyanine (Tinolux BBS) was added to 20g of 75 wt% solution of a di-(hydrogenated tallow) dimethyl ammonium chloride (sold under the trade name "Querton 442" by Keno-Gard). The mixture was agitated gently.

A water insoluble quaternary ammonium salt of the phthalocyanine was extracted into carbon tetrachloride. The carbon tetrachloride solution was washed with water, dried, and the carbon tetrachloride was removed by evaporation.

The solid product recovered from the carbon tetrachloride was added to water (1 l) and stirred vigorously with a high speed mixer for several minutes. This removed any residual water soluble material which might have been carried over from the starting material. The solid product was recovered by filtration and the washing step was continued until the filtrate was colourless.

The washed solid dissolved in carbon tetrachloride, dried and the carbon tetrachloride was removed by evaporation. A dark blue solid product was obtained. This was a novel photobleach composition in accordance with the present invention.

Preparation of a laundry detergent

A pre-dispersion of the water-insoluble photobleach was made up by dispersing the required amount of photobleach in a micellar solution of an alkyl ethoxylate of HLB in the range 11-14.

A liquid laundry detergent containing the photobleach material prepared above was prepared by agitating sufficient of the pre-dispersion with a conventional heavy duty laundry liquid composition containing anionic and non-ionic surfactants to give a concentration of 0.05 %wt.

Comparative Test A

A liquid laundry detergent was prepared having the same composition as that prepared in Example 1 except that it did not contain the novel photobleach but contained 0.05% wt of the water-soluble phthalocyanine photobleach ("Tinolux BBS") used as starting material in Example 1.

Comparative Test B

A liquid laundry detergent was prepared having the same composition as that prepared in Example 1 except that it did not contain any photobleach.

Testing the detergent compositions

Spotting

1 ml of the liquid detergent prepared as in Example 1 was applied to a piece of white cotton cloth. Sufficient time was allowed for the liquid detergent to soak into the cloth. The detergent was rinsed off

under a stream of cold water, and the cloth was then dried. No blue stain attributable to the photobleach could be seen on the cloth.

The spotting test was repeated with the detergent of comparative test A. A noticeable blue-green strain as left on the cloth even after prolonged rinsing.

Washing

2.5g of the liquid detergent composition of Example 1 was added to 500ml of water at 60° C. Two standard cotton cloth swatches stained with red wine (each 100mm X 100mm)(EMPA) were added to the liquid. After 15 minutes the swatches were removed and rinsed with cold water. One of the swatches was dried while illuminated with a 50 W quartz-halogen lamp mounted at 150mm from the cloth swatch (to simulate the effect of sunlight). The cloth was rewetted from time to time with distilled water. The other cloth was allowed to dry in normal ambient laboratory lighting.

The amount of stain removl was estimated by measuring the reflectance of the fabric before and after washing.

Drying conditions	% stain removal
ambient lighting	21
quartz-halogen	41

The washing and drying test was repeated using the detergent of comparative Test B. The results were:

Drying conditions	% stain removal
ambient lighting	21
quartz-halogen	27

A comparison of the result for Example 1 and comparative Test A clearly shows the improved spotting performance of the photobleach of the invention. A comparison of the results obtained for Example 1 and Comparative Test B clearly shows that the material of the present invention is still an effective photobleach, despite being insoluble in pure water.

Claims

1. A photobleach which is a substantially water-insoluble photobleach substantially free from water-soluble photobleach.

2. A photobleach according to claim 1 which is derived from a water-soluble photobleach which is an anionically substituted porphine.

3. A photobleach according to either of the preceding claims which is metallated.

4. A photobleach according to claim 3 which is metallated with aluminium.

5. A photobleach according to any one of the preceding claims which is a phthalocyanine.

6. A photobleach according to any one of the preceding claims which is a salt of a water-soluble photobleach quaternary nitrogen compound having one or two C_{10}-C_{22} alkyl groups.

7. A photobleach which is a salt of di(hydrogenated tallow) dimethyl ammonium chloride.

8. A process for making a substantially water-insoluble photobleach which comprises:

(i) reacting a water-soluble photobleach with a long chain alkyl quaternary nitrogen compound to precipitate an insoluble reaction product, and

(ii) washing the reaction product with water to remove water-soluble reactants.

9. A process according to claim 8 wherein the insoluble reaction product is extracted from an aqueous reaction medium with a hydrophobic solvent, which is subsequently removed, before being subjected to the

water washing step.

10. A process according to either one of claims 8 or 9 wherein the quaternary nitrogen compound is a quaternary nitrogen having one or two C_{12}-C_{15} alkyl groups.

11. A process according to any one of claims 8 to 10 wherein the quaternary nitrogen compound is a quaternary ammonium compound.

12. A process for making a liquid laundry detergent which comprises

(i) reacting a water-soluble photobleach with a long chain alkyl quaternary nitrogen compound to precipitate an insoluble reaction product,

(ii) washing the reaction product with water to remove water-soluble reactants,

(iii) preparing a pre-dispersion of the water-insoluble photobleach using a non-ionic surfactant, and

(iv) adding the pre-dispersion to a liquid laundry detergent composition.

13. A laundry detergent composition which comprises a substantially water-insoluble photobleach according to any one of claims 1 to 7.

14. A laundry detergent composition according to claim 10 wherein the water-insoluble photobleach is made by a process according to any one of claims 8 to 11.

15. A laundry detergent according to either of claim 13 to 14 which is a liquid laundry detergent.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 90300349.9

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.⁵)
A	EP - A1 - 0 087 833 (UNILEVER NV) * Page 2, lines 4-10; page 4, lines 9-20; page 7, lines 1-16 *	1-7, 12,13	C 11 D 3/395 D 06 L 3/04 C 09 B 47/32
D,X	US - A - 2 150 741 (HARRISON) * Claims; column 1, lines 39-50 *	8-11	
A	EP - A1 - 0 035 470 (CIBA-GEIGY AG) * Claims 1-10; page 17, lines 12-27 *	1-7, 12,13	
A	EP - A1 - 0 054 992 (UNILEVER NV) * Page 3, lines 20 - page 5, line 8; page 22, line 24 - page 23, line 12 *	1-6, 12,13	
D,A	US - A - 4 166 718 (REINERT) * Claims 1,2; column 7, lines 41-46 *	1-6,13	TECHNICAL FIELDS SEARCHED (Int Cl.⁵) C 11 D D 06 L C 09 B
A	DE - A1 - 3 410 611 (CIBA-GEIGY AG) * Claims 1,9-15,17,19,21; pages 7,8 *	1-6,13	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	28-03-1990	SCHÄFER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO Form 1503. 03.82